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# EFFECTS OF PROCESSING CONDITIONS ON THE PHYSICAL AND ELECTROCHEMICAL PROPERTIES OF CARBON AEROGEL COMPOSITES

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## ABSTRACT

The carbon aerogel/carbon paper composites have physical properties similar to those of monolithic carbon aerogels but do not require supercritical extraction during fabrication. The resorcinol-formaldehyde based carbon aerogel phase is intertwined between the fibers of a commercial carbon paper. The resulting composites have variable densities (0.4-0.6 g/cc), high surface areas (300-600 m<sup>2</sup>/g), and controllable pore sizes and pore distribution. The effects of the resorcinol-formaldehyde concentrations (50-70% w/v) and the pyrolysis temperature (600-1050°C) were studied in an attempt to tailor the aerogel microstructure and properties. The composite physical properties and structure were analyzed by transmission electron microscopy and multipoint-BET analyses and related to electrochemical capacitive data in 5M KOH. These thin carbon aerogel/carbon paper composite electrodes are used in experiments with electrochemical double-layer capacitors and capacitive deionization.

## INTRODUCTION

Thin carbon aerogel/carbon paper composites are attractive materials for many applications, most notably, as electrodes in electrochemical double-layer capacitors [1] and capacitive deionization [2, 3]. These high-density composites (>0.4 g/cc) have high electrical conductivity (20-100 S/cm), high surface areas (200-500 m<sup>2</sup>/g) and favorable microporous structure (average pore diameter, 40-200Å). The carbon aerogel phase in the composite is derived from an organic aerogel precursor made by the aqueous polycondensation of resorcinol (1,3-dihydroxylbenzene) and formaldehyde. In contrast to monolithic microporous aerogels which are supercritically dried (with CO<sub>2</sub>), the composite organic aerogel is generally air dried. These high-density cross-linked gels have sufficient strength to retain a large fraction of the porous structure from collapsing due to capillary forces associated with solvent evaporation. The simpler preparation procedure makes the composite aerogel materials more economically attractive than monolithic samples.

While extensive work has been done with monolithic resorcinol-formaldehyde (RF) aerogels and their carbon derivatives [4-8], studies on carbon composite materials have

been limited. Only results with high-density materials ( $> 0.5$  g/cc) have been reported [3,9]. With the current development of commercial electrochemical devices using thin carbon aerogel composites, the availability of these types of electrode materials with a wide range of properties are desirable.

This collaborative effort investigates two changes in the processing conditions of the composite materials. The effects of the resorcinol-formaldehyde concentration and the pyrolysis temperature (600-1050°C) are studied to tailor the composite structure and properties. Results of these effects on the materials properties and their electrochemical capacitive behavior are reported.

## EXPERIMENTAL

*Carbon aerogel/carbon paper composites* - The preparation of composite electrode materials containing RF aerogels integrated into a commercial carbon paper has been described before [9]. In general, resorcinol (1,3 dihydroxybenzene) and formaldehyde were mixed in a 1:2 molar ratio, respectively. Deionized/distilled water was added as the diluent and sodium carbonate as the base catalyst. A porous carbon paper (0.127-mm thick, Lydall Technical Papers, Rochester, NH) was soaked with the catalyzed-RF solution and placed in between two glass plates. The impregnated sample was cured at room temperature, 50°C and 85°C successively for one day each at the various temperatures. The cured composite was then soaked in a copious amount of acetone and subsequently dried at room temperature. Care had to be taken to assure that the pore water was adequately exchanged with acetone. Finally, the RF/carbon paper composite was heat treated at 1050°C in a nitrogen atmosphere for two hours to pyrolyze the RF component. Table 1 lists several monolithic and composite samples and their characteristics. Conventional high-density monolithic and composite RF materials (samples M1, M2 and C1) were prepared with RF concentrations between 50-70% weight per volume (w/v) using a molar ratio of resorcinol to catalyst (sodium carbonate) of 200.

A number of the carbon aerogel composite materials were commercial products obtained from Ocellus, Inc. (San Carlos, CA). These materials were prepared in a similar procedure as described above except with modified formulation and drying steps. The solvent (acetone) exchange step was eliminated in this case and the pore fluid (water) was dried directly at ambient conditions. The concentration of resorcinol-formaldehyde was varied between 50 to 70% weight per volume (w/v) at a constant resorcinol to catalyst molar ratio. After curing and drying, the resulting RF composites were then pyrolyzed under an inert atmosphere using a temperature ramp of 8 to 13 hours duration, depending on the final pyrolysis temperature (between 600 and 1050°C.) Electrode materials were then tested directly without any additional treatment.

*Electrochemical capacitance measurements* - Electrochemical studies were performed using a 64-channel Maccor battery tester. Experiments were done using circular (4.5-cm diameter) Teflon cells. The two identical 1.5-cm diameter electrodes were separated by 2 pieces of Whatman fiberglass filter papers (934-AH). Nickel foils were used as current

collectors in sodium hydroxide (5M KOH) electrolytes. The whole assembly is sandwiched between 2 Teflon plates and held together by 0.6-cm diameter Teflon screws. Electrolyte filling was accomplished via three successive evacuation (2 psi) and pressurization (24.5 psi) stages in approximately 30 minutes. The assembly and testing of aqueous cells were carried out under ambient conditions. The charge/discharge experiments were carried out at constant currents (25 mA) to 0.85 and 1 V upper limits for 40 cycles. The capacitance,  $C$ , was determined by dividing the discharge capacity,  $Q$ , by the charging voltage,  $V$ . The total dry weight and volume of the two carbon electrodes were used in the capacitance density calculations.

*Physical characterization* - The BET surface area and pore size distribution were obtained using a five-point  $N_2$  gas adsorption technique (Micromeritics ASAP 2000). The average pore size and pore size distribution were determined from the desorption branch according to a theory developed by Barrett, Joyner, and Halenda (the BJH method) [10]. The composite morphology and microstructure was also examined by scanning (Hitachi S570) and transmission electron microscopy (JEM-200CX).

## RESULTS AND DISCUSSION

*Carbon resorcinol-formaldehyde aerogel composite* - Table 1 compares the difference in properties and specific capacitances between monolithic and composite RF carbon aerogels. Selected information on monolithic materials with formulation comparable to the range studied in this work are summarized in Table 1 as the basis for comparison with those for composite materials. More extensive data on monolithic carbon aerogels can be found in the literature [4-8]. Supercritically-dried monolithic carbon aerogels showed the most desirable properties. Surface areas typically range from 400-1000  $m^2/g$  and thermally treated samples can have BET surface areas as high as 3000  $m^2/g$ . Specific capacitance in 5M KOH electrolytes was as high as 35 F/g [9]. On the other hand, thin, air-dried carbonized RF composites tend to have lower surface areas. The samples from this study as well as several similar materials from other work [9, 11, 12] show BET surface areas between 200-600  $m^2/g$ , a reduction of about 40% from supercritically-dried monolithic samples. Nevertheless, the thin composite and the supporting carbon paper matrix apparently prevent a total collapse of the pore network during ambient temperature drying. At sufficiently high-density ( $>0.4$  g/cc) a fraction of the bulk is rigid and should retain a microporous structure, even in subsequent pyrolysis. The pore size and distribution are adequate (see Table 1) for double-layer formation. The electrochemical capacitive measurements in 5M KOH show specific capacitance values in the range of 17-19 F/g (see table 1). These values are also consistent with those obtained from other samples.

*Effects of resorcinol-formaldehyde sol concentration* - A series of samples with different concentration of resorcinol-formaldehyde in the gel was prepared to study the effect of density on the properties and microstructure. The concentration of the dissolved solids (resorcinol and formaldehyde) was varied between 50 to 70% (weight/volume) at a constant resorcinol/catalyst molar ratio. The results are shown in Table 1. Samples C52 and C62 (at 50 to 60 %w/v, respectively) show high BET surface areas with reasonable

large average pore sizes. High-resolution transmission electron microscopy show porous structure with average pore diameters in the same range with values reported in Table 1. Our initial investigations with Raman spectroscopy reveal a small up-shift in the Raman frequencies in the aerogel/paper composites compared to the monolithic materials. Some broadening of the graphite peak

**Table 1.** List of carbon aerogels and their characteristics

Samples	Aerogel type	R-F content, % wt./vol	Density, g/cc	BET area, m <sup>2</sup> /g	Average pore size, Å	Specific capacitance, F/g
M1 <sup>a</sup>	monolithic	40	0.58	666	65	34
M2 <sup>a</sup>	monolithic	50	0.83	580	50	28
C1	composite	70	0.6	360	80	17
C52	composite	50	0.41	389	170	17.8
C62	“	60	0.47	408	56	19.0
C72	“	70	0.60	297	37	0.9
C600	“	60	0.40	623	77	14.9
C700	“	60	0.43			23.0
C800	“	60	0.43	589	77	28.4
C900	“	60	0.45			25.8
C1050	“	60	0.44	399	61	17.8

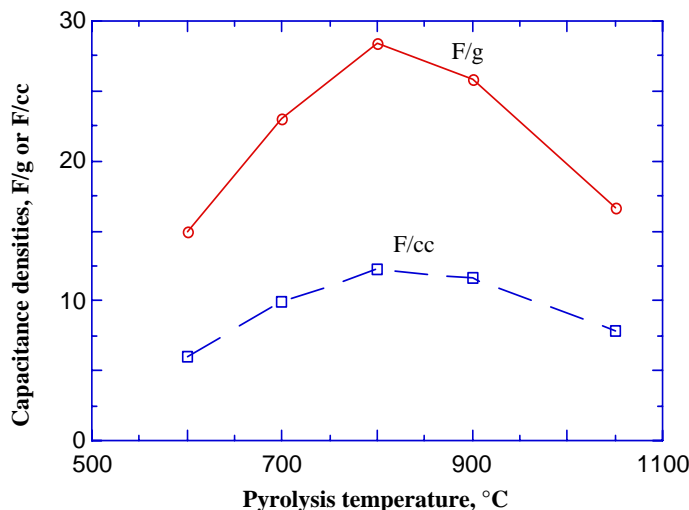
<sup>a</sup> data from references 8 and 9.

(1603 cm<sup>-1</sup>) and the disordered-induced peak (1350 cm<sup>-1</sup>) was evident. The in-plane crystallite sizes ( $L_a$ ) for composite aerogels are 20-30% larger than the value of 25 Å reported for monolithic aerogels [9]. Additional discussion on the microstructure of these materials will be reported in future communications. The specific capacitances for C52 and C62 samples (see Table 1) were 17.8 and 19 F/g, respectively.

The sample with an RF content of 70% w/v, C72, was apparently affected by a significant structure change (including pore collapse). While the standard procedure (sample C1 in Table 1) with acetone exchange prior to drying apparently was successful in preserving the porous structure, the direct drying of this similar high-density sample was not effective here. A smaller average pore size and an abundance of micropores (< 20 Å) were observed. Such a structure apparently could not form a double-layer and thus yield a low capacitance. A comparable result was observed with two batches of similarly-prepared samples. Transmission electron microscopy shows evidence of highly interconnected particles with limited pore volume. The simple air drying of the pore water, which did not appear critical for the two lower-density samples, was detrimental at this RF content. The reason for this variation in the effects of the drying conditions is not obvious at this point. Additional study is being considered.

*Effects of pyrolysis temperature between 600 to 1050°C* - Another important means for controlling the structure and properties of carbon aerogels is by changing the pyrolysis temperature. Figure 1 shows the specific and volumetric capacitance densities of a series of composite materials (C600-C1050) as a function of pyrolysis temperature. Both curves show a peak capacitance near 800°C. The trend here is in agreement with an earlier study with monolithic carbon aerogels [9]. The peak specific capacitance of 29 F/g was the highest ever observed for composite electrode materials. This value approaches those obtained from monolithic samples as seen in Table 1. Considering the drastic change in processing conditions (air dried vs. supercritical extraction), the performance improvement is significant. Higher energy densities can be expected from capacitors using these modified electrodes.

Several characterization experiments including gas adsorption analysis, transmission electron microscopy and Raman spectroscopy are being conducted to obtain additional information on these materials. Surface areas may be the critical factor for this increased



**Figure 1.** Specific and volumetric capacitance densities (F/g and F/cc, respectively) of RF carbon aerogel composites as a function of pyrolysis temperature.

capacitance as observed for the sample pyrolyzed at 800°C (*e.g.*, 589 m<sup>2</sup>/g). A question remains on the contribution of the pseudo-capacitive components to the electrochemical activities of these electrodes. Continued cycling of C800 (Table 1) electrodes in 5 M KOH was carried out to study the reversibility of the capacitive behavior and to elucidate irreversibility arising from any pseudo-capacitive redox reactions. Stable capacities (over 650 cycles) at constant current charge/discharge conditions at two voltage limits of 0.85 V and 1 V suggest that the carbon surface remains unchanged under these cycling conditions.

## CONCLUSIONS

The results demonstrate that sufficiently high-surface-area carbon aerogel composites can be prepared with a simple air drying procedure. Electrode materials with different

properties can be prepared by changing the processing conditions. Composites pyrolyzed at 800°C showed capacitances approaching those of monolithic materials. The availability of these materials with high electrochemical capacitance is expected to improve the energy densities of supercapacitors and electrosorptive capacities of electrochemical deionization cells.

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